Compliments
John White Jr

SULPHON-FLUORESCEÏN

AND OTHER

SULPHON-PHTHALEÏNS.

DISSERTATION

PRESENTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

JOHN WHITE, JR.

1891.

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ACKNOWLEDGMENT.

It gives the author of this dissertation much pleasure to express his most sincere thanks to Professor Remsen, at whose suggestion the work here described was undertaken, and under whose immediate supervision it has been prosecuted, and to whom he will ever be indebted for the instruction received at his hands. He also desires to express his thanks to Drs. Morse and Renouf for valuable instruction in chemistry, and to Dr. Williams, under whom the course in mineralogy and geology was pursued.

ON SULPHON-FLUORESCEÏN AND OTHER SULPHON-PHTHALEÏNS.

Introductory and Historical.

Ortho-sulpho-benzoic acid and its derivatives have been the subject of investigation in this laboratory for several years. The special study of those derivatives which contain phenol residues, and are hence related to the phenol-phthaleïns, was begun in 1884, when Remsen[1] made the discovery that when ortho-sulpho-benzoic acid is heated with resorcin a fluorescent substance is obtained. The investigation was, however, not carried farther at that time. In 1887 Remsen and Hayes[2] took up the work, and prepared a compound which they supposed to be the first of the class of sulphon-phthaleïns. Their method of preparation consisted in heating together ortho-sulpho-benzoic acid and resorcin to a temperature of 178°–185°, when reaction took place, the mass becoming quite viscous after having been heated for some time. The product, after purification, was analysed for sulphur and water, results being obtained which led them to ascribe to it the constitutional formula $C\begin{cases} C_6H_3<^{OH}_{O} \\ C_6H_3<_{OH} \\ C_6H_4.SO_2 \\ O\text{—}\lrcorner \end{cases}$, because of its analogy to von Baeyer's fluoresceïn: $C\begin{cases} C_6H_3<^{OH}_{O} \\ C_6H_3<_{OH} \\ C_6H_4.CO \\ O\text{—}\lrcorner \end{cases}$.

On preparing the barium salt of this compound, they found that the analyses showed a percentage of barium somewhat above that required by a compound of the formula $(C_{19}H_{13}O_7S)_2Ba$. The work was interrupted at this point.

[1] Am. Chem. J. **6**, 180. [2] Ibid. **9**, 372.

Shortly after, Remsen and Linn[1] took up the work with the hope of clearing up the subject. They soon made an observation which led to an explanation of the difficulties previously encountered. While making an analysis of the supposed ortho-sulpho-benzoic acid, Linn noticed that, during the fusion with caustic potash, according to the Liebig method for determining sulphur, a strong odor of ammonia was given off. This led him to suspect that the substance he was dealing with, instead of being ortho-sulpho-benzoic acid, was the ammonium salt of that acid.

He made a considerable quantity of it according to the method of Brackett and Hayes,[2] and subjected it to a careful investigation. He found it to be indeed the acid ammonium salt of ortho-sulpho-benzoic acid of the formula $C_6H_4<^{COOH}_{SO_2ONH_4}$, formed from benzoic-sulphinide, as has since been shown by Remsen and Burton,[3] in accordance with the following equations:

1. $C_6H_4<^{CO}_{SO_2}>NH + H_2O = C_6H_4<^{COOH}_{SO_2NH_2}$,

2. $C_6H_4<^{COOH}_{SO_2NH_2} + H_2O = C_6H_4<^{COOH}_{SO_2ONH_4}$.

Instead, therefore, of using ortho-sulpho-benzoic acid in the preparation of their supposed sulphon-fluoresceïn, Remsen and Hayes had used the acid ammonium salt of the acid.

After making the discovery above referred to, Remsen and Linn repeated the experiment of Remsen and Hayes, and proved that the substance obtained was, instead of sulphon-fluoresceïn, the ammonium salt of dioxybenzoyl-benzene-sulphonic acid, the reaction taking place according to the equation:

$$C_6H_4<^{COOH}_{SO_2ONH_4} + C_6H_4<^{OH}_{OH} = C_6H_4<^{CO.C_6H_3(OH)_2}_{SO_2.ONH_4} + H_2O.$$

The acid itself has since been prepared and investigated by C. C. Blackshear, of this laboratory, the results being published in his dissertation (1890).

Remsen and Linn[4] found that when dioxybenzoyl-benzene-sulphonic acid is heated for several hours at 120°, it is gradually converted into a dark-brown substance which dissolves in alkalies, forming intensely fluorescent solutions. Von Baeyer had shown

[1] Am. Chem. J. **11**, 73. [2] Ibid. **9**, 399. [3] Ibid. **11**, 403. [4] Loc. cit.

that when dioxybenzoyl-benzoic acid is heated, either alone or with resorcin, it is converted into fluoresceïn. They thought it highly probable, therefore, that a like reaction took place in this instance, and that the product obtained was the long sought-for sulphon-fluoresceïn, and this it proved to be. They showed that the conversion of dioxybenzoyl-benzene-sulphonic acid into sulphon-fluoresceïn by heat is represented by the equation:

$$2(OH)_2C_6H_3.CO.C_6H_4.SO_2OH = C_{19}H_{12}O_6S + C_6H_4\begin{matrix}COOH\\SO_2OH\end{matrix} + H_2O.$$

The fact that ortho-sulpho-benzoic acid is one of the products of the decomposition was shown by boiling the filtrate from the solid sulphon-fluoresceïn with barium carbonate; the barium salt of ortho-sulpho-benzoic acid was thus obtained, the analyses giving figures corresponding with the formula

$$C_6H_4\begin{matrix}CO.O\\SO_2.O\end{matrix}>Ba + 2H_2O.$$

Analyses of the sulphon-fluoresceïn thus obtained made by Linn, and subsequently by Blackshear, show that the composition is represented by $C_{19}H_{12}O_6S + H_2O$, though they were unable to determine from the facts known whether the water given off is water of constitution or of crystallisation. They consider, however, that the simplest view is that the compound has the structure represented by the formula $C\begin{cases} C_6H_3\begin{matrix}OH\\OH\end{matrix} \\ C_6H_3\begin{matrix}OH\\OH\end{matrix} \\ C_6H_4.SO_2 \\ O\text{——}\end{cases}$, and that by loss of water it is converted into the anhydride analogous to fluoresceïn, viz. $C\begin{cases} C_6H_3\begin{matrix}OH\\O\end{matrix} \\ C_6H_3\begin{matrix}OH\\\end{matrix} \\ C_6H_4.SO_2 \\ O\text{——}\end{cases} + H_2O$. When this is dissolved in an alkali, a salt of the tetra-hydroxyl compound is probably formed.

It can readily be seen, from the brief history of sulphon-fluoresceïn, which has just been given, that very little is known of the class of compounds known as the sulphon-phthaleïns, of which sulphon-fluoresceïn is the first that has been described; moreover,

that of sulphon-fluoresceïn itself little more is known than the constitution, which is based on analyses, the method of formation and analogy to known compounds. It therefore seemed highly desirable that the investigation of the subject should be carried further; and it was for this purpose—the study of the compounds themselves, of their derivatives and decompositions—that the work described in these pages was undertaken, and, although there yet remains much to be done, it is hoped that the results here recorded may be of value, as adding something to the knowledge of a very interesting subject.

Preparation of sulphon-fluoresceïn from dioxybenzoyl-benzene-sulphonic acid.—The method used was that described by Remsen and Linn.[1] The dioxybenzoyl-benzene-sulphonic acid was placed in a test-tube and heated in a sulphuric-acid bath. By means of a thermometer placed in the test-tube the temperature could be noted, and the mass could at the same time be stirred from time to time; a quite advantageous precaution, since by frequent stirring the reaction takes place much more rapidly. The temperature of the bath was allowed to rise gradually; at about 100°–110° the acid melts, the liquid thus formed being of a dark-red color; this rapidly becomes darker, and, when the temperature is raised to 160°–170°, at which the reaction takes place most readily, it becomes a deep brown; the mass meanwhile becomes quite viscous, and a considerable amount of water is given off. After heating for several hours the reaction is at an end. The mass was allowed to become cool, then was treated with cold water and filtered, the sulphon-fluoresceïn remaining on the filter was thoroughly washed with cold water to remove the ortho-sulpho-benzoic acid formed as one of the products of the reaction:

$$2(OH)_2C_6H_3.CO.C_6H_4.SO_2OH =$$

$$C\begin{cases} C_6H_3<\begin{matrix}OH\\O\end{matrix} \\ C_6H_3<OH \\ C_6H_4.SO_2 \\ O\text{---}\lrcorner \end{cases} + C_6H_4<\begin{matrix}COOH\\SO_2OH\end{matrix} + H_2O.$$

It was then dissolved in alkalies, a moderately concentrated solution of caustic potash being used for this purpose. This solution is intensely fluorescent, even when extremely dilute, and is

[1] Loc. cit.

of a pale yellow color in transmitted light. The alkaline solution, after filtration, was treated with dilute acid, when the sulphon-fluoresceïn was precipitated as a reddish-brown flocculent precipitate; this was washed a few times by decantation, then on the filter with the aid of the pump.

Sulphon-fluoresceïn is very difficultly soluble in hot alcohol and in hot glacial acetic acid. It is more easily soluble in hot than in cold water, though but slightly soluble in either. It dissolves with great ease in alkalies, forming the intensely fluorescent solutions spoken of above.

Action of bromine on sulphon-fluoresceïn.—Von Baeyer[1] found that when fluoresceïn is treated with bromine, three substitution-products are obtained, according to the proportion of bromine used, monobrom-fluoresceïn, dibrom-fluoresceïn, and tetrabrom-fluoresceïn (eosin). He was unable to obtain the tribrom-fluoresceïn. Of these he only succeeded in isolating in pure condition the dibrom- and tetrabrom-fluoresceïns, and from the latter a number of well-defined salts were obtained.

In the case of sulphon-fluoresceïn, the principal action of bromine is to form the *dibrom-sulphon-fluoresceïn*, and probably a *monobrom-sulphon-fluoresceïn*. The tribrom- and tetrabrom-substitution-products could not be obtained. Dry sulphon-fluoresceïn was suspended in four or five times its weight of glacial acetic acid in a small beaker; to this was added a twenty-per cent. solution of bromine in glacial acetic acid, in the proportion of one molecule of bromine to one of sulphon-fluoresceïn. Reaction immediately took place, the liquid becoming warm from the reaction, and fumes of hydrobromic acid being given off. A solid product was thus obtained, somewhat lighter in color than the original sulphon-fluoresceïn. It was filtered off, washed with glacial acetic acid, in which it is much less soluble than in water, and placed in a desiccator containing solid caustic potash to remove the last traces of acetic acid. The bromine product is slightly soluble in alcohol and water. It is insoluble in ether, chloroform, glacial acetic acid and petroleum ether. In alkalies it dissolves readily, forming strongly fluorescent solutions, which show a very decided pink in transmitted light, very like that produced by eosin. Estimations of sulphur and bromine gave the following results:

[1] Ann. Chem. **183**, 36.

I. 0.1195 gram substance gave 0.0550 gram $BaSO_4$ (Liebig).
II. 0.1596 gram substance gave 0.0782 gram AgBr (Carius).

	Calculated for $C_{19}H_{11}BrO_6S$.	Found.
S	7.17	6.32
Br	17.88	20.85

It was concluded from these results that some dibrom-sulphon-fluoresceïn had been formed at the same time as the monobrom-product, and that a mixture of the two was thus obtained. It was then decided to prepare other bromine substitution-products of sulphon-fluoresceïn, to see if some of these could be prepared in pure condition.

With this in view, sulphon-fluoresceïn was treated with two molecules of bromine in the manner described above. The action was in every respect similar to that described in the preceding experiment, except that in this case, after standing for a short time, the whole mass became almost solid, and the reaction appeared to take place more readily than in the previous case. The product obtained was very like that obtained in the first experiment, but appeared to be more granular, and was hence easier to wash. The following analyses were obtained:

I. 0.1187 gram substance gave 0.0526 gram $BaSO_4$ (Liebig).
II. 0.0772 gram substance gave 0.0509 gram AgBr (Carius).
III. 0.0903 gram substance gave 0.0600 gram AgBr (Carius).
IV. 0.29685 gram substance, heated for three hours at 160°, lost 0.00951 gram H_2O.

	Calculated for $C_{19}H_{10}Br_2O_6S + H_2O$.	Found. I.	II.	III.	IV.
S	5.89	6.09	...	...	...
Br	29.39	...	28.06	28.27	...
H_2O	3.30	...	...	...	3.20

The bromine in this product appears to be somewhat lower than that required for dibrom-sulphon-fluoresceïn, and as there was not enough of the material left for a complete analysis, another preparation was made in the same manner. This was, however, left over night on the filter in contact with some glacial acetic acid. The following morning it was noticed that it had become very much darker and was harder and more brittle; it was decided, however, to analyse this product, but, as the results show, it had evidently undergone some change.

I. 0.1646 gram substance gave 0.2984 gram CO_2 and 0.0528 gram H_2O.

II. 0.2357 gram substance gave 0.4138 gram CO_2 and 0.0689 gram H_2O.

III. 0.2561 gram substance gave 0.4522 gram CO_2 and 0.0751 gram H_2O.

	Calculated for $C_{19}H_{10}Br_2O_6S + H_2O$.	Found. I.	II.	III.
C	41.91	49.44	47.88	48.16
H	2.21	3.57	3.25	3.26

The results were not at all satisfactory, but, as the amount of material at hand was limited, it was thought better to proceed with other experiments rather than to attempt to prepare the dibrom product in pure condition.

Three molecules of bromine were next added to one molecule of sulphon-fluoresceïn. The action took place as in previous experiments. Estimations of sulphur and bromine gave the following results:

I. 0.1240 gram substance gave 0.0504 gram $BaSO_4$ (Liebig).

II. 0.0919 gram substance gave 0.0611 gram AgBr (Carius).

	Calculated for $C_{19}H_9Br_3O_6S$.	Calculated for $C_{19}H_{10}Br_2O_6S + H_2O$.	Found. I.	II.
S	5.30	5.89	5.59	...
Br	39.65	29.39	...	28.29

Another product was prepared by treating sulphon-fluorescein with four molecules of bromine. Reaction took place at once, with copious evolution of fumes of hydrobromic acid.

An analysis of the product gave the following figures:

I. 0.1810 gram substance gave 0.2883 gram CO_2 and 0.0476 gram H_2O.

II. 0.2768 gram substance gave 0.4293 gram CO_2 and 0.0733 gram H_2O.

III. 0.1325 gram substance gave 0.0533 gram $BaSO_4$ (Liebig).

IV. 0.2175 gram substance gave 0.0918 gram $BaSO_4$ (Liebig).

V. 0.0703 gram substance gave 0.0466 gram AgBr (Carius).

	Calculated for $C_{19}H_{10}Br_2O_6S + H_2O$.	I.	II.	Found. III.	IV.	V.
C	41.91	43.44	42.30	...	...	...
H	2.21	2.93	2.94	...	...	...
Br	29.39	...	...	...	...	28.21
S	5.89	...	...	5.52	5.76	...

It appears probable, from a consideration of the results obtained, that the principal product of the action of bromine on sulphon-fluoresceïn is a *dibrom-sulphon-fluoresceïn*, but that, owing to the difficulty attending the separation of the products formed in the reaction, it cannot be obtained in pure condition. The dibrom-substitution-product may be mixed with one or more of the other bromine products, or perhaps the action is not complete, and this is evidenced by the fact that the analyses for bromine, while agreeing very well for the various preparations, are too low in all cases; the carbon and hydrogen are likewise too high. This is what would be expected if the substance were a mixture of the dibrom-substitution-product, with some undecomposed sulphon-fluoresceïn. The facts at hand are not, however, sufficient to justify a final statement on this point.

Action of acetic anhydride on dibrom-sulphon-fluoresceïn.—It was hoped that a method of separation of the dibrom-product from other products of the action of bromine on sulphon-fluoresceïn might be found in the acetyl derivative. With this in view, some of the bromine product, obtained by treating sulphon-fluoresceïn with four molecules of bromine, was heated with an excess of acetic anhydride in a small flask, provided with an inverted condenser; the flask was placed in a bath of sulphuric acid and the temperature was kept at 140°. There appeared to be only a very slight action.

Another experiment was made, the mixture being heated in a sealed tube at 180°–200° for several hours. The tube was examined from time to time to ascertain if the action was complete. The reaction took place very slowly, about sixteen hours being required for its completion. The product thus obtained was a dark green, almost black, liquid. This was treated with an excess of alcohol to convert the acetic anhydride remaining into the ester; after evaporating the solution to dryness a black substance remained. This is brittle, has a greenish sheen, and is insoluble in alkalies, even when warmed with them on the water-bath. The alkali was removed with acid, and the insoluble product was purified by washing. An analysis for sulphur gave the following result:

0.1179 gram substance gave 0.0312 gram $BaSO_4$ (Liebig)= 3.63 per cent. S.

The calculated percentage of sulphur for a diacetyl-dibrom-sulphon-fluoresceïn is 5.25. The analysis and the general appearance and behavior of the substance indicated that it was an impure product. A second attempt to prepare an acetyl derivative of the bromine product was not more successful, and the further study of the action of bromine on sulphon-fluoresceïn was discontinued, owing to the limited amount of material at disposal. It appears quite probable, however, that at least one, and possibly more, bromine-substitution-products may be obtained in comparatively pure condition.

Action of phosphorus pentachloride on sulphon-fluoresceïn.— When sulphon-fluoresceïn is treated with phosphorus pentachloride (1 : 2), no reaction takes place at the ordinary temperature, but when warmed on the water-bath a very slight action is noticed. This action takes place quite readily at a temperature of 125°–130°; the mass becomes darker in color and semi-liquid. When a test, made by treating a small portion of this with alkali, shows no fluorescence, the reaction is at an end. The temperature must be kept moderately low while decomposing the excess of phosphorus pentachloride, as the sulphon-fluoresceïn-chloride is somewhat soluble in hot water. The solid product thus obtained was washed free from compounds of phosphorus by decanting a few times and then washing on the filter, using suction to facilitate the washing. As thus prepared the product obtained has a bright-red color, soluble to some extent in alcohol and in alkalies. The solution in alkalies first assumes a deep cyanide-blue color, which upon standing soon changes to a deep green, then to a pale yellow, and finally becomes nearly colorless. No fluorescence is observed in any of these stages of change.

An analysis gave the following results:

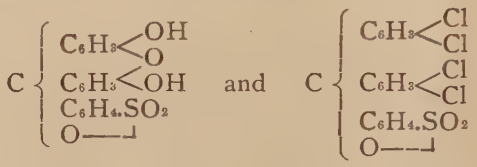
I. 0.2319 gram substance gave 0.4076 gram CO_2 and 0.0601 gram H_2O.

II. 0.1712 gram substance gave 0.0783 gram $BaSO_4$ (Liebig).

III. 0.2108 gram substance gave 0.2131 gram AgCl (Carius).

	Calculated for $C_{19}H_{10}Cl_2O_4S$.	Calculated for $C_{19}H_{10}Cl_4O_3S+H_2O$.	Found. I.	Found. II.	Found. III.
C	56.29	47.71	47.94	...	...
H	2.47	2.52	2.88	...	...
Cl	17.51	29.67	...	...	25.05
S	7.91	6.71	...	6.29	...

The results are not satisfactory, especially those obtained for chlorine and sulphur. As for the chlorine determination, it may be said that it was found that the decomposition of the substance was not complete, hence the chlorine came low. Unfortunately, the small amount of the chloride obtained did not permit another estimation of either chlorine or sulphur, and the time at disposal was not sufficient for the preparation of more material. This is especially to be regretted, since there is undoubted evidence that a definite product was obtained. The facts at hand point to the conclusion that when sulphon-fluoresceïn is treated with phosphorus pentachloride, four chlorine atoms enter in, replacing the anhydride oxygen as well as the phenol hydroxyls, the product bearing this relation to sulphon-fluoresceïn:



Action of acetic anhydride on sulphon-fluoresceïn.—An attempt was made to prepare an acetyl derivative of sulphon-fluoresceïn by heating it with an excess of acetic anhydride. In the first experiment the heating was conducted at 140° in a small flask provided with an inverted condenser. The sulphon-fluoresceïn went gradually into solution, but upon examination it was evident that there had been very slight action; it therefore seemed best to heat in sealed tubes. This was done, the tube being kept at a temperature of 180°–200° for about six hours. After cooling, the product contained in the tube was found to consist of a reddish-colored, semi-viscous liquid. This was poured into an excess of alcohol, and when this solution was evaporated, a black powder was obtained. This powder dissolves in alkalies with a faint red color, the solution showing a dirty green fluorescence. From the alkaline solution it is precipitated upon addition of acids, separating out as a flaky brown precipitate.

I. 0.1934 gram substance gave 0.4643 gram CO_2 and 0.0816 gram H_2O.

II. 0.1017 gram substance gave 0.0467 gram $BaSO_4$ (Liebig).

	Calculated for $C_{23}H_{16}O_8S$.	Found. I.	II.
C	61.05	65.47	...
H	3.55	4.71	...
S	7.09	...	6.31

The result indicates that the product is evidently not a diacetyl-sulphon-fluoresceïn, and as other attempts to obtain such a product were equally fruitless, it did not seem profitable to continue investigation in this direction. It may be said in this connection that, judging from the results obtained in the case of sulphon-fluoresceïn and of the bromine derivative, as well as in that of other compounds closely related to them, especially those described by Blackshear in his dissertation, an acetyl derivative of this class of compounds is not readily formed, or, if formed, it is probably decomposed again to some extent during subsequent treatment.

Reduction of sulphon-fluoresceïn.—Upon warming sulphon-fluoresceïn with sodium hydroxide and zinc-dust, the liquid gradually loses its color, thus showing that reduction takes place. The sulphon-fluoresceïn formed by the reaction could not be obtained, for upon filtering the solution from the excess of zinc-dust, oxidation immediately takes place, as is indicated by the color of the solution, sulphon-fluoresceïn being formed. An attempt was made to obtain it by extracting with ether, but the same difficulty was met with.

Action of nitric acid on sulphon-fluoresceïn.—When sulphon-fluoresceïn is treated with cold fuming nitric acid, action immediately takes place, the sulphon-fluoresceïn is dissolved, and a deep red liquid is formed. From this, however, nothing is precipitated upon the addition of water. The character of the reaction was of such a nature that further investigation did not seem advisable.

Action of resorcin on dioxybenzoyl-benzene-sulphonic acid.—It has been shown that the conversion of dioxybenzoyl-benzene-sulphonic acid into sulphon-fluoresceïn by heat is represented by the equation

$$2(HO)_2C_6H_3.CO.C_6H_4.SO_2OH = C\left\{\begin{array}{l} C_6H_3\!<\!\begin{array}{l}OH\\O\end{array} \\ C_6H_3\!<\!OH \\ C_6H_4.SO_2 \\ O\text{——}\end{array}\right. + C_6H_4\!<\!\begin{array}{l}COOH\\SO_2OH\end{array} + H_2O.$$

The yield of sulphon-fluoresceïn is far from quantitative. Now, as ortho-sulpho-benzoic acid is the sulphur analogue of phthalic acid, and since fluoresceïn is obtained by heating phthalic acid or phthalic anhydride with resorcin, it was thought to be possible to prepare sulphon-fluoresceïn in a similar manner by heating ortho-sulpho-benzoic acid with resorcin, or, as bearing more directly upon the case here cited, it was thought that by heating dioxybenzoyl-benzene-sulphonic acid with resorcin the yield of sulphon-fluoresceïn would be increased and the loss of ortho-sulpho-benzoic acid prevented. With this in view the following experiments were performed:

Dioxybenzoyl-benzene-sulphonic acid was heated with resorcin (1:1). The reaction took place quite readily at 150°–160°; after heating about two hours the mass became so viscous as to prevent stirring. After the mass had become cold it was observed that it was of a different color from that of sulphon-fluoresceïn, and that it was much more brittle. It was washed with water, dissolved in caustic potash, reprecipitated by dilute sulphuric acid, filtered and washed. The dry product was almost black in color; it was hard and quite brittle.

0.0805 gram substance gave 0.0410 gram $BaSO_4$ (Liebig) = 7.00 per cent. S.

The theoretical percentage of sulphur for sulphon-fluoresceïn is 8.29. Another portion was converted into the bromine substitution-product; an estimation of sulphur gave:

0.1614 gram substance gave 0.0492 gram $BaSO_4$ (Liebig) = 4.19 per cent. S, whereas the percentage required by dibrom-sulphon-fluoresceïn is 6.09.

From these results it appears that the action does not take place in the manner supposed; that the resorcin acts on the ortho-sulpho-benzoic acid, not to form sulphon-fluoresceïn, but something different, and the product obtained is a mixture of sulphon-fluoresceïn with this other substance. It was then decided to study the action of resorcin on ortho-sulpho-benzoic acid in order to find out what substances are formed.

Preparation of ortho-sulpho-benzoic acid.—The method used was that described by Remsen and Dohme.[1] It consists in boiling commercial saccharin, or benzoic sulphinide, with dilute hydro-

[1] Am. Chem. J. **11**, 332.

chloric acid in a large balloon-flask provided with an inverted condenser. Within the course of one or two hours all of the sulphinide was converted into the acid ammonium salt of ortho-sulpho-benzoic acid, as was indicated by the disappearance of the sweet taste. The reaction takes place in two stages, as was shown to be the case by Remsen and Burton:[1]

1. $C_6H_4\begin{matrix}CO\\SO_2\end{matrix}>NH + H_2O = C_6H_4\begin{matrix}COOH\\SO_2NH_2\end{matrix}$.

2. $C_6H_4\begin{matrix}COOH\\SO_2NH_2\end{matrix} + H_2O = C_6H_4\begin{matrix}COOH\\SO_2ONH_4\end{matrix}$.

The solution containing the acid ammonium salt was filtered from the insoluble para-sulphamine-benzoic acid, which constitutes about fifty per cent. of the commercial saccharin; the filtrate was evaporated to dryness on the water-bath. To obtain the acid, the acid ammonium salt was treated with phosphorus pentachloride, when the chloride of ortho-sulpho-benzoic acid was formed, thus:

$$C_6H_4\begin{matrix}COOH\\SO_2ONH_4\end{matrix} + 2PCl_5 = C_6H_4\begin{matrix}COCl\\SO_2Cl\end{matrix} + 2POCl_3 + NH_4Cl + HCl.$$

The chloride was washed with cold water to remove compounds of phosphorus, and then boiled with water in a flask with inverted condenser, the chloride being by this means converted into the acid:

$$C_6H_4\begin{matrix}COCl\\SO_2Cl\end{matrix} + 2H_2O = C_6H_4\begin{matrix}COOH\\SO_2OH\end{matrix} + 2HCl.$$

The acid thus prepared was further purified by recrystallisation.

During the process of the conversion of the chloride into the acid by boiling with water, a curious substance was obtained, which, as it seems to have escaped the observation of earlier investigators of this subject, it may be well to call attention to. Soon after the water begins to boil, lenticular crystals collect on the sides of the flask, and, as the boiling is continued, these disappear and a considerable quantity of a white sublimate collects in the condenser. By reversing the condenser this is carried over by the water-vapor.

The substance thus obtained is a white crystallised compound, which has a very peculiar odor, not disagreeable in dilute form,

[1] Loc. cit.

but having a persistent character which makes it unpleasant. The substance is insoluble in concentrated acids, and may be heated with them without undergoing decomposition. A very concentrated solution of caustic potash has no effect on it. It is not readily soluble in alcohol, but dissolves with great ease in ether, and from the ethereal solution, by taking proper precautions, it may be obtained as a well-crystallised substance which melts sharply at 113°. Under certain conditions the ethereal solution undergoes spontaneous transformation, a pale-yellow oil being obtained which has a sharp acid odor. It contains phosphorus and chlorine. The properties here described agree so closely with those given for that most remarkable substance, *chlorphosphuret of nitrogen*, that there can be little doubt that they are one and the same compound. This substance was discovered by Liebig and Wöhler.[1] It was afterwards investigated by Gladstone[2] and also by Wichelhaus.[3] A determination of its molecular weight gives it the formula $P_3N_3Cl_6$. It is formed by the action of ammonia on phosphorus pentachloride, and by the action of chlorine on ammonium chloride; thus its formation in this instance is easily accounted for.

Action of resorcin on ortho-sulpho-benzoic acid.—Fahlberg and Barge[4] describe some experiments performed by them relative to the action of resorcin on ortho-sulpho-benzoic acid. They found that when ortho-sulpho-benzoic acid is heated with either 2 or 4 molecules of resorcin, a condensation-product is obtained containing four resorcin residues. They ascribe to it the formula $C_{31}H_{20}O_8S + 4H_2O$, and give the following analyses:

	Calculated for $C_{31}H_{20}O_8S + 4H_2O$.	Found. I.	II.	III.	IV.
C	59.60	59.12	59.04	59.68	...
H	4.50	...	4.97	4.91	...
S	5.13	5.24	5.05	5.38	5.34
H_2O	11.54	11.42	...	11.20	11.38

As there were very few or no details given and no further investigation made, it seemed desirable, especially since it is in line with the series of investigations which have been carried on in this laboratory for some years past, to repeat the work of Fahlberg and Barge, and also to see if other phenol residues might be intro-

[1] Ann. Chem. **11.**
[2] Chem. Soc. Qu. J. **11**, 121.
[3] Berichte **3**, p. 163.
[4] Ibid. **22**, 765.

duced in the same way; hence the experiments described below were undertaken.

I.—Ortho-sulpho-benzoic acid and resorcin (1 : 4) were heated together in a sulphuric-acid bath. The temperature was allowed to rise gradually; at 100°–110° the mixture melted to a deep-red liquid, which gradually grew darker as the temperature rose. At 140° reaction took place, bubbles were seen to pass up through the liquid, water was given off, and in the course of a few hours the mass became quite viscous and dark in color. The product thus obtained was, when cold, hard, quite brittle, and of a reddish-brown color, somewhat different from that of sulphon-fluoresceïn. The physical properties of the substance are worthy of comment. When rubbed it shows electrical phenomena; when treated with water in the cold it softens to a slight extent, then becomes hard again, the process being similar to the setting of plaster of paris or of cement; this is even more noticeable if it is heated with water. At the boiling-point of water it is a soft, dark-green mass, of the consistency of tar, and floats on the surface of the water. Upon cooling the mass becomes hard and brittle and sinks in the water. When the mass is heated in an air-bath to a temperature of 120° the same phenomenon is noticed. This change in physical condition does not appear to be attended by any change in chemical composition. The substance dissolves quite readily in alkali, forming an intensely fluorescent solution, but the fluorescence is of a different character from that of sulphon-fluoresceïn. The solution is of a deep-red color in concentrated form, showing a delicate pink in dilute form, while, as before stated, sulphon-fluoresceïn shows a yellow color in dilute solution.

It is precipitated from the alkaline solution by acids, and for purposes of purification this method was used. The precipitate is flaky, and very difficult to wash thoroughly. After purification it was carefully examined. It is easily soluble in alcohol and ether, insoluble in chloroform, water, petroleum ether, and in cold glacial acetic acid, slightly soluble in warm. Analysis gave the following results:

I. 0.1110 gram substance gave 0.2623 gram CO_2 and 0.0560 gram H_2O.

II. 0.1416 gram substance gave 0.3365 gram CO_2 and 0.0750 gram H_2O.

III. 0.0981 gram substance gave 0.0304 gram $BaSO_4$ (Liebig).

IV. 0.1559 gram substance gave 0.0450 gram $BaSO_4$ (Liebig).

The tabulated results are:

	I.	II.	III.	IV.
C	64.45	64.81	...	...
H	5.61	5.89	...	...
S	...	...	4.26	3.97

A second series of analyses, made somewhat later, gave these results:

I. 0.2231 gram substance gave 0.5281 gram CO_2 and 0.0990 gram H_2O.

II. 0.1703 gram substance gave 0.0428 gram $BaSO_4$ (Liebig).

III. 1.2564 grams substance, heated for four hours at 140°, lost 0.0788 gram H_2O.

IV. 0.6253 gram substance, heated for five hours at 140°, lost 0.0404 gram H_2O.

	I.	II.	III.	IV.
C	64.56	...	...	...
H	4.93	...	...	...
S	...	3.45	...	...
H_2O	...	...	6.27	6.46

It will be observed that there is a very marked difference in the percentage of hydrogen obtained in the second series from those obtained in the first. The same thing will be observed in the case of the second preparation, which will shortly be described. The cause for this was found to lie in the fine chromate mixture which was used for combustions. This, though it had been dried in preparation, by long standing had absorbed moisture, which was reckoned as hydrogen in the final results.

II.—A second preparation was made in the same manner (as before described), and the product obtained was found to be quite similar to the first. Analysis gave these results:

I. 0.1469 gram substance gave 0.3503 gram CO_2 and 0.0851 gram H_2O.

II. 0.1173 gram substance gave 0.0362 gram $BaSO_4$ (Liebig).

	I.	II.
C	65.03	...
H	6.45	...
S	...	4.24

A second series of analyses was made in which *dry* chromate mixture was used.

I. 0.1712 gram substance gave 0.4054 gram CO_2 and 0.0706 gram H_2O.

II. 0.7668 gram substance, heated for four hours at 140°, lost 0.0384 gram H_2O.

III. 0.2790 gram substance, heated for five hours at 140°, lost 0.0156 gram H_2O.

	I.	II.	III.
C	64.59	...	...
H	4.58	...	...
H_2O	...	5.01	5.59

III.—A third preparation, in which four molecules of resorcin were used, was then obtained.

0.1837 gram substance gave 0.0550 gram $BaSO_4$ (Liebig) = 4.11 per cent. S.

On comparing the results here recorded with those given by Fahlberg and Barge, it will be seen that there is a wide difference, and this difference is of such a nature as not to be accounted for on the supposition that the substance contains four resorcin residues, but indicates rather that a condensation takes place between one molecule of ortho-sulpho-benzoic acid and *six* molecules of resorcin. This is brought out more clearly in the table below:

	Calculated for $C_{31}H_{20}O_8S + 4H_2O$ (Fahlberg & Barge) (4 mol. resorcin).	Calculated for $C_{48}H_{28}O_{10}S + 3\frac{1}{2}H_2O$. (6 mol. resorcin).	Found. Preparation. I.				Prep. II.			Prep. III.
			I.	II.	III.*	IV.	I.	II.*	III.	
C	59.60	64.57	64.45	64.81	64.56	..	65.03	64.59	..	..
H	4.50	4.39	5.61	5.89	4.93	..	6.45	4.58	..	..
S	5.13	4.01	4.26	3.97	3.45	..	4.24	..	..	4.11
H_2O	11.54	7.88	..	..	6.27	6.46	..	5.01	5.59	..

The asterisk * marks the results obtained when a *dry* chromate mixture was used. If, then, those results for hydrogen, in which this precaution was not observed, be discarded, it will easily be seen that the facts point very strongly to the conclusion that the substance contains six resorcin residues.

Having arrived at these conclusions, it was then decided to make several preparations, using six molecules of resorcin instead of four. Three such preparations were obtained. The method used for their formation was the same as that described in the preceding experiments. Analyses of these products gave:

Preparation I.

I. 0.2176 gram substance gave 0.5177 gram CO_2 and 0.0944 gram H_2O.

II. 0.1345 gram substance gave 0.0362 gram $BaSO_4$ (Liebig).

III. 1.3625 grams substance, heated for four hours at 140°, lost 0.0820 gram H_2O.

Preparation II.

I. 0.2655 gram substance gave 0.0752 gram H_2O (combustion).

II. 0.1744 gram substance gave 0.0436 gram $BaSO_4$ (Liebig).

III. 1.2358 grams substance, heated for four hours at 140°, lost 0.0675 gram H_2O.

Preparation III.

0.2559 gram substance gave 0.6115 gram CO_2 and 0.1153 gram H_2O.

	Calculated for $C_{42}H_{28}O_{10}S + 3\frac{1}{2}H_2O$.	Found. Prep. I. I.	Prep. I. II.	Prep. I. III.	Prep. II. I.	Prep. II. II.	Prep. II. III.	Prep. III.
C	64.57	64.93	...	...	...	...	...	65.17
H	4.39	4.82	...	...	4.98	...	...	5.01
S	4.01	...	3.70	...	...	3.44	...	...
H_2O	7.88	...	...	6.02	...	...	5.46	...

It will be observed that in all cases the estimations of water of crystallisation are low. An explanation of this will be offered later.

The results obtained do not agree as well as could be wished, but, considering the nature of the substance and the difficulty attending its purification, this is not surprising.

Since it was difficult to decide between several formulas—some containing six resorcin residues, with varying amounts of water of crystallisation; others containing four resorcin residues, but which contain much less water than that ascribed to it by Fahlberg and Barge—it seemed desirable to analyse the dehydrated substance, as the differences between the tetra and hexaresorcin-derivatives are more marked. After heating for several hours at 140°, the residues were analysed:

Product I_4[1].

I. 0.1188 gram substance gave 0.2966 gram CO_2 and 0.0587 gram H_2O.

[1] The suffixes 4 and 6 refer to the preparations made by using four and six molecules of resorcin respectively.

II. 0.1320 gram substance gave 0.3317 gram CO_2 and 0.0569 gram H_2O.

III. 0.1130 gram substance gave 0.0285 gram $BaSO_4$ (Liebig).

IV. 0.1374 gram substance gave 0.0364 gram $BaSO_4$ (Liebig).

Product II_4.

I. 0.1393 gram substance gave 0.3462 gram CO_2 and 0.0542 gram H_2O.

II. 0.1018 gram substance gave 0.0302 gram $BaSO_4$ (Liebig).

III. 0.1258 gram substance gave 0.0398 gram $BaSO_4$ (Liebig).

Product III_6.

I. 0.1224 gram substance gave 0.3078 gram CO_2 and 0.0439 gram H_2O.

II. 0.1208 gram substance gave 0.0289 gram $BaSO_4$ (Liebig).

Product IV_6.

I. 0.1379 gram substance gave 0.3459 gram CO_2 and 0.0566 gram H_2O.

II. 0.1195 gram substance gave 0.0283 gram $BaSO_4$ (Liebig).

III. 0.1492 gram substance gave 0.0353 gram $BaSO_4$ (Liebig).

Upon comparing these results with those calculated for substances containing four and six molecules of water, the following table will show that they are more in accord with those required by a substance containing six resorcin residues.

	Calculated for $C_{24}H_{20}O_8S$ (4 Resorcin).	Calculated for $C_{42}H_{36}O_{10}S+H_2O$ (6 Resorcin).	Found. Prep. I_4.		Prep. II_4.		Prep. III_6.	Prep. IV_6.	
			I.	II.	I.	II.		I.	II.
C	67.38	68.41	68.10	68.62	67.78	..	68.58	68.41	..
H	3.63	3.98	5.49	4.79	4.33	..	3.99	4.56	..
S	5.80	4.25	3.47	3.64	4.08	4.34	3.29	3.26	3.25

It appears from this that all the water of crystallisation is not driven off at 140°, but that there still remains one molecule. This would explain the low results in the previous determinations of water, for it will be seen from a study of those results that the difference between the percentages found and the calculated is just about what is required for one molecule of water. An attempt was made to drive off this last molecule of water. The temperature of the air-bath was allowed to rise gradually above 140°, and weighings made from time to time showed a gradual loss in weight. When a temperature of 180° was reached a surprising observation was made. Upon removing the weighing-tube con-

taining the substance from the bath, and passing it close to the nose, a strong odor of sulphuretted hydrogen was noticed. A test was made with silver nitrate and with lead acetate solutions, both of which gave the characteristic reaction for hydrogen sulphide. This was an entirely unaccountable decomposition, and one for which no explanation can be offered.

Taking all the facts into consideration, it appears that the subject is an extremely difficult one to deal with, owing to the nature of the substance, the difficulties attending its purification and separation from other substances of like kind, and the peculiar behavior under the influence of heat. It may be said, however, that the facts point to the conclusion that when ortho-sulpho-benzoic acid is heated with either four or six molecules of resorcin, a condensation-product containing *six* resorcin residues is obtained.

With the desire to determine if the hexa resorcin-derivative of ortho-sulpho-benzoic acid is the only product of the action of resorcin on the acid, an experiment was made in which a smaller proportion of resorcin was used than in the preceding experiments. In this case only two molecules of resorcin were used. The experiment was performed in a manner entirely similar to the preceding, and the product obtained had the same general appearance and similar properties to that previously described. Upon making an analysis, however, it was soon apparent that this was a different substance, thus:

I. 0.1690 gram substance gave 0.4060 gram CO_2 and 0.0671 gram H_2O.

II. 0.1701 gram substance gave 0.0697 gram $BaSO_4$ (Liebig).

III. 0.3434 gram substance, heated for four hours at 150°, lost 0.0101 gram H_2O.

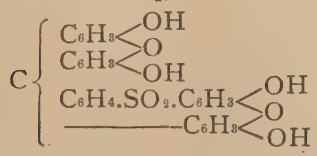
The figures thus obtained agree very closely with those calculated for a product containing *four* resorcin residues, but containing less water than that described by Fahlberg and Barge:

	Calculated for $C_{31}H_{20}O_8S + 4H_2O$ (Fahlberg and Barge).	Calculated for $C_{31}H_{20}O_8S + H_2O$.	Found. I.	Found. II.	Found. III.
C	59.60	65.24	65.52	...	...
H	4.50	3.86	4.42	...	...
S	5.13	5.62	...	5.63	...
H_2O	11.54	3.16	...	...	2.94

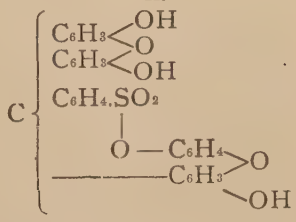
It must be said that these facts are rather surprising, considering the fact that when an attempt was made to prepare a derivative of ortho-sulpho-benzoic acid containing four resorcin, by using four molecules of resorcin for its preparation, instead a derivative containing six molecules of resorcin was obtained. However, this is not more surprising than that a derivative containing four resorcin residues should be obtained when two molecules of resorcin, the exact amount required to form sulphon-fluoresceïn, are used. It appears as if the tendency is always toward the formation of the higher derivatives, but that this is influenced to some extent by the relative masses of the substances present. It is to be regretted that the time at disposal was not sufficient to permit the further investigation of this extremely interesting point. So much time was necessarily consumed upon the earlier investigation that this particular study had to be dropped at this point.

According to the facts at hand, then, we conceive the formation of the three resorcin-derivatives of ortho-sulpho-benzoic acid, viz., *the diresorcin derivative* (sulphon-fluoresceïn), *the tetraresorcin derivative*, and *the hexaresorcin derivative*. It may be fairly stated that the constitution of the first of these has been pretty definitely determined. For the second, the tetraresorcin derivative, preferably called *tetraresorcino-sulphon-phthaleïn*, Fahlberg and Barge[1] offer three possibilities represented by the three formulas:

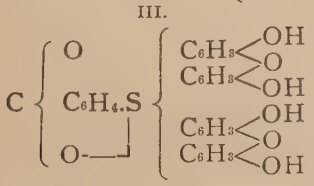
I.



II.



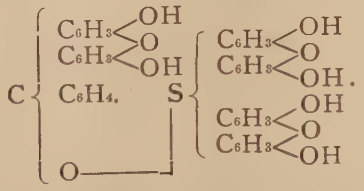
III.



Of these formulas I and II represent the anhydride oxygen of ortho-sulpho-benzoic anhydride $C_6H_4<^{CO}_{SO_3}>O$, as replaced by

[1] Loc. cit.

two resorcin residues. Von Baeyer[1] proved that this is not the way in which the action takes place in the formation of the phenolphthaleïns from phthalic anhydride and the phenols. It therefore seems probable that formula III is more in accord with the facts. Applying the same reasoning to the hexaresorcin derivative (*hexaresorcino-sulphon-phthaleïn*), it may be said that the constitution is most probably represented by the formula:



Thus the series is complete. Should, however, the anhydride oxygen be conceived to be replaced by resorcin residues, other possibilities present themselves, and the formation of other compounds might be expected.

Action of bromine on hexaresorcino-sulphon-phthaleïn.—The dry, powdered hexaresorcino-sulphon-phthaleïn suspended in glacial acetic acid was treated with bromine (1 : 2), a twenty-per cent. solution of bromine in glacial acetic acid being used for the purpose. Action took place at once, as was evidenced by the copious evolution of fumes of hydrobromic acid. After standing for some time the solid portion was filtered off from the liquid, and washed with glacial acetic acid until no more bromine or hydrobromic acid was observed. The amount obtained was so small as not to admit of an analysis. It shows the characteristic eosin color in alkaline solution. It appears to be more soluble in glacial acetic acid than the bromine substitution-product of sulphon-fluoresceïn, for upon addition of water to the filtrate a beautiful red precipitate was obtained, which exhibited the same characteristics as the solid matter first collected.

Action of phosphorus pentachloride on hexaresorcino-sulphon-phthaleïn.—Hexaresorcino-sulphon-phthaleïn was treated with phosphorus pentachloride (1 : 6) in a small Erlenmeyer flask. No action took place at the ordinary temperature, or even when heated on the water-bath. When, however, the mixture was

[1] Ann. Chem. **202**, 36.

heated in a sulphuric-acid bath to a temperature of 120°–130°, it soon became semi-liquid and dark-colored. After heating thus for a short time, the flask was removed from the bath, and the excess of phosphorus pentachloride was decomposed with water, the flask meanwhile being kept cool, as the product is soluble in hot water. The residue, a dark-red substance, was then washed free from phosphorus compounds and examined. It dissolves in alkali, forming a green solution about the color shown by chromous compounds in solution; from this solution it is reprecipitated by acids. If, however, the alkaline solution is allowed to stand, the green color gradually changes to yellow, and then the precipitate formed by acids no longer appears like the original substance, but is much lighter, almost white in color. No analysis was made of the substance.

Action of acetic anhydride on hexaresorcino-sulphon-phthaleïn.—An attempt was made to prepare an acetyl derivative by heating together hexaresorcino-sulphon-phthaleïn and acetic anhydride in a closed tube. The mixture was heated for several hours at 160°, and upon examining the tube it was found to contain a thin black liquid. When this was poured into an excess of alcohol a black precipitate was formed; this was filtered off, and the alcoholic solution evaporated to a small volume, when more of it was obtained. This black substance dissolves in alkalies, forming fluorescent solutions suspiciously like that formed by hexaresorcino-sulphon-phthaleïn. It was dissolved in glacial acetic acid, in which it is quite soluble, but this solution was evaporated almost to dryness without obtaining a residue; when, however, water was added, a yellowish-colored, flaky precipitate was obtained. This was analysed for sulphur, but though several trials were made only a trace of sulphur could be obtained. Nothing further was done with it, and the investigation was discontinued at this point.

A few experiments relative to the action of other phenols on ortho-sulpho-benzoic acid and on its acid ammonium salt will now be briefly described. They are offered merely as a few simple preliminary tests, the time at disposal not being sufficient for complete investigations.

Action of phenol on the acid ammonium salt of ortho-sulpho-benzoic acid and on ortho-sulpho-benzoic acid.—It has been shown

that when resorcin is heated with the acid ammonium salt of ortho-sulpho-benzoic acid, one resorcin residue enters in place of the acid hydroxyl, forming the acid ammonium salt of dioxybenzoyl-benzene-sulphonic acid; and when heated in like manner with the acid, various resorcino-sulphon-phthaleïns are formed. It seemed desirable to try the action of phenol, as well as of other more complex phenols, on these two substances, to see if similar products could be obtained.

I. The acid ammonium salt of ortho-sulpho-benzoic acid was heated with phenol (1:1) in a sulphuric-acid bath to a temperature of 110°–120°. The mixture melted at about 90° to a clear red liquid, but no reaction took place. When a dehydrating agent, stannic chloride, was added, reaction began shortly after the mixture had melted; the mass soon became more viscous and assumed a brilliant scarlet color, due to the formation of small needles having that color. The reaction does not appear to increase to any extent after the first few minutes. The mass was boiled with water to drive off the excess of phenol and precipitate the tin as hydroxide; the precipitation is rendered complete by adding a little sodium carbonate; the filtrate was evaporated and a small quantity of a reddish-colored substance was obtained, but not in sufficient quantity for analysis. It dissolves easily in alcohol and in water, both solutions being of a fine deep-red color. Upon the addition of a few drops of alkali to either of these solutions a magnificent purple color is obtained, showing no fluorescence. Acids change the purple color to a pale yellow, but produce no precipitation.

II. When ortho-sulpho-benzoic acid was heated with phenol alone no reaction took place, but when stannic chloride was used a very slight reaction was observed. On heating these substances together in a sealed tube at 160° for 6–8 hours, a viscous, reddish-brown liquid was obtained. This was removed by boiling with water. The solution was freed from excess of phenol and tin by first boiling, then precipitating the tin with sodium carbonate. When an acid was added to the alkaline solution a very finely divided black precipitate was obtained. This, after thorough washing, was examined. It is purple in alkaline solution, changed to pale yellow by acids. The color appears very sensitive and suggests its use as an indicator. The substance was evidently not a pure product, and no analysis was made.

Action of pyrogallol on the acid ammonium salt of ortho-sulpho-benzoic acid and on ortho-sulpho-benzoic acid.—I.—No reaction takes place between pyrogallol and the acid ammonium salt of ortho-sulpho-benzoic acid when the two are heated without the use of a dehydrating agent. When, however, stannic chloride is added, the mixture first melts to a red liquid at 70°–90°, and when a temperature of 110° is reached, reaction sets in, the mass soon becomes dark in color and quite viscous. A temperature of 130°–140° was maintained for four hours, after which the mass was removed from the vessel. It was black, glutinous, and was insoluble in water, alkalies and alcohol. It was not possible then to separate it by the ordinary methods from the tin salts. The substance did not present a very attractive appearance, and as it was evidently impure, no analysis was attempted.

II.—When ortho-sulpho-benzoic acid is heated with pyrogallol (1 : 6) to a temperature of 140°–160°, a reaction takes place, the mass soon becomes viscous and quite dark. After heating for 4–6 hours the mass was removed from the vessel. It is a dark-colored, glutinous substance, which dissolves in alkalies, forming a very deep indigo-blue solution; from this it is precipitated by acids, separating out as a dark, flaky substance. This precipitate is of such a nature as to make its washing a matter of great difficulty; the glutinous mass packs on the filter, so that the liquid will not pass through. The substance has properties quite similar to those of galleïn, described by von Baeyer. It dissolves quite easily in alkalies, forming the blue solution spoken of above. Upon standing a few minutes this color disappears, changing to a reddish brown; acids also produce the same change.

The substances here described, though difficult to obtain in pure condition, are nevertheless well worth investigation, since they present very interesting characteristics.

Conclusion.

The following facts are perhaps worthy of mention:

I. It appears quite probable that when sulphon-fluoresceïn is treated with bromine, the chief product of the action is the formation of a dibrom-substitution-product.

II. That phosphorus pentachloride substitutes both the hydroxyl groups and the anhydride oxygen with chlorine.

III. It is not possible to prepare sulphon-fluoresceïn by the

action of resorcin on ortho-sulpho-benzoic acid, but that, instead, more resorcin enters into combination, forming the more complex derivatives, tetraresorcino-sulphon-phthaleïn and hexaresorcino-sulphon-phthaleïn, which possess the same general properties as sulphon-fluoresceïn.

IV. Acetyl derivatives of this class of compounds are obtained with great difficulty, or perhaps cannot be prepared at all, since all the efforts thus far made to obtain them have proved unsuccessful.

The further examination of the sulphon-phthaleïns presents an interesting subject for other investigations. The study of the action of other phenols on ortho-sulpho-benzoic acid promises to be attended with success.

Biographical.

The author of this dissertation, John White, Jr., was born on February 24, 1866, in Montgomery County, Maryland. He received his early education in the public schools of the State. In 1882 he entered the Academy at Charlestown, West Virginia, where he spent two years in preparation for college. He entered the Johns Hopkins University in the fall of 1884, and pursued the undergraduate course in that institution, receiving his A. B. degree in June, 1888. Since that time he has pursued the study of chemistry, with mineralogy and geology as subsidiaries. In June, 1890, he was appointed a Fellow in Chemistry, which honor he has held during the past year.